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**Question 82: In light of coming benzene regulations, are you using (or planning to use) the isomerization unit for benzene conversion? How does this affect isomerization catalyst performance and unit operation? How does this affect the gasoline pool? How does benzene saturation in an isomerization unit compare to a dedicated benzene saturation reactor/catalyst?**

**ZMICH (UOP LLC)**

This question relates very well with Question #80 that we discussed a few minutes ago, and what I'd like to do is touch upon some of the key points that we mentioned there. So Item #1 on the slide relates to the naphtha isomerization units being flexible in their ability to handle benzene. Typically, 3% benzene in the feed and in a range of 0 vol% to 5 vol% is normal. For item #2, as benzene increases, the reactor temperature increases because of the heat of reaction, decreasing the research octane number or the PIN. The higher temperature means lower isomerization or lower iso ratio. Also, as benzene increases, it poisons more of the catalyst in the reactor, which effectively is increasing the space velocity across the reactor, forcing one to operate at a higher average reactor inlet temperature, which drives the reactor outlet temperature up and pushes the RON or the PIN number down. Item #3: As I mentioned before, a chloride alumina catalyst system typically operates up to 5 vol%. The last item: For an Isom process unit containing less than 5%, we can add a saturation reactor upstream of that, revamp a typical Isom unit by adding a saturation reactor, to be able to handle up to 30 vol% benzene up to and greater than 30 vol% benzene in the feed.

**KAISER (Delek Refining Ltd.)**

As an operator of a refining company and facing the MSAT II regulations, the objective is clearly stated: You need to get the benzene out of the gasoline pool. There are two ways to do it: You can either extract it or you can turn it into something else. When we approach the problem, we started out with the extraction route. But as a small refiner far enough from any potential sales sources or consumption sources for benzene, extraction is not going to be an economic choice for us. We'd be a small producer and a high cost producer, and it's likely that a lot of the refiners that are extracting now are going to be increasing their volumes. There are probably even going to be other refiners who are not currently making benzene that are going to start. And so for us, extraction is kind of out the window.

We turn, then, to saturation and there are two choices there. You can do kind of a post-treatment saturation plant where the benzene has already been made and you're trying to destroy it. Or, you can do a pretreat-type option where you take the benzene precursors in your reformer feed and you try to isomerize those to get some octane boost, but it reduces the amount of benzene that you produce.

The other thing that we're considering and wanting to do as much as possible, because this is an environmentally driven project with technically no return, is that we want to be able to reuse as much equipment as we have. We do have this idle isomerization unit, as I've stated before. Being able to reuse those assets and minimize our capital investment, again, minimizes the financial impact upon the refinery itself.

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So the things that we've done: We've been looking at our reformer feed splitter to see what we can do there. Are we going to be able to push enough of the benzene precursors out of the reformer feed to get the benzene content low enough in the reformat.

And then, once we see

Gasoline Processes Gasoline Processes Isomerization-Benzene • Light paraffin isom units flexible to handle benzene? Benzene ?? T ? RON? Benzene ? effective LHSV ? RON • Penex™ unit to 5% benzene • Penex Plus capable >30% benzene  
whether or not we can get away with that, what is the feed to the isomerization look like? Is it too heavy? Is there too much benzene in there? Are there too many heavies in there? Is it just totally worthless as isomerization feed? If we start looking at the backend of the reformer, if we take a light cut or a hard cut of the reformat, what does that look like for an Isom feed? Is there too much benzene in there? Are we going to install a dedicated saturation bed? Is the equipment that we have going to be sufficient for that? You couple that with the fact that to saturate benzene, it takes 4,500 scfb of hydrogen to saturate the benzene. Now we're looking at hydrogen balance within the refinery between all of our other hydrotreaters and the production off of our Platformer. And the fact that ethanol has reduced the need to run higher severity on the reformer for gasoline octane, there's a potential that we'll be running the reformer for hydrogen and not for octane. So this becomes a very convoluted situation, and we're trying to minimize capital investment.

The other thing that we're seeing recently with some other projects that we've accomplished is that for major pieces of equipment—reactors, vessels, compressors, heaters, we're looking at 52 weeks of delivery. So just a warning for everyone out there, if you haven't already started on this and you don't already know what you're going to do, you're out of time. You need to figure it out right now because between six months of engineering, a year of procurement, and six months of construction, it's 2011.

### **QUINTANA (Valero Energy Corporation)**

Joe and Allen have covered this very well already. As we've indicated earlier, we can handle up to 5% benzene in an Isom unit with a dedicated lead saturation reactor. The specific limitation for any given unit is determined by the inter-reactor cooling capacity and the lag reactor performance target. As Joe was further indicating, you can go to higher levels of benzene in the feed, but you may need to recycle some low benzene product to dilute the feed benzene if you are beyond the per-pass limit on the saturation reactor inlet. We should note also the impact on hydrogen consumption that Allen has covered. We also see that many of our reformers in the future are likely to be driven by the refinery hydrogen balance. And given the excess octane in the future, we're going to likely see a fair amount of octane giveaway as a result of that.

Now if you do convert your Isom unit to saturation alone, one possible benefit is that it could eliminate some chloride-related corrosion issues, so you may get some reliability improvements as a result.

I like most of the things that the panel has discussed here. One of the things I really want to ask a question about is: If we are looking at a feed benzene level of 5%, typically what might be the x factor for the feed? I think one of the concerns we have is with the 5% benzene content feed. There could be up to about 100°F exotherm in the lead reactor and the refiner could be incapable of operating with a 5% benzene feed.

### **KAISER (Delek Refining Ltd.)**

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Yes, earlier when we were talking about the 5% benzene in the feed and up to 8% benzene-plus, I don't remember exactly what the X factor of that was, but it was significant enough to impact the overall yields on that isomerization unit. That's something that you'll need to work with your technology provider on once you've decided pre-fractionation, post-fractionation. They'll need to do yield projections for you on that and account for the very high exotherms that you will see in that lead isomerization reactor because it does have a large impact on your isomerate yields and what they look like.

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